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FURTHER STUDIES ON THE MECHANISM OF THERMAL DECOMPOSITION OF SOME RELATED QUINOLINE METAL CHELATES IN THE SOLID STATE

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ABSTRACT

The mechanism of thermal decomposition of chelates of 8-aminoquinoline and 8-hydroxyquinoline with copper in an air atmosphere has been studied by thermal analysis (TG and DTA). An analysis of the results obtained strongly suggests some differences in the mechanism of thermal decomposition of 8-hydroxyquinoline (8HQ) from that of 8-aminoquinoline (8AQ) complexes with copper(II). These are indicative of the nature of the two metal ligand bonds in both complexes. Finally, a stepwise thermal decomposition character for the materials investigated was developed for the first time.

INTRODUCTION

The majority of compounds, including complexes, suffer physical and chemical changes such as changes in weight and calorific values, when subjected to heat energy. In differential thermal analysis (DTA) investigations, overlapping processes can be distinguished more easily than in the thermogravimetric (TG) method. Therefore, the DTA method is very useful for investigations of the qualitative type, while TG, based on gravimetry, is more suited for quantitative work. The stability constant of the Pd complex with 2-methyl-8-hydroxyquinoline (8HQ) was evaluated, and the TG, DTA and magnetic properties of the precipitated $Pd(C_{10}H_8NO)_2$ complex have been studied [1]. The stability constants of Cu(II), Ni(II) and Co(II) of the 8-quinoline derivatives were determined at 25 °C [2] indicating that the complexes of the methyl-substituted ligands are less stable than the corresponding complexes of unsubstituted ligands, the stability decreased due to the steric repulsions of the 2-methyl group. From thermal studies on Al(III)-2-methyl-8HQ and Al(III)-2,5-dimethyl-8HQ, Khwaja and Ali [3] noted that these chelates were less stable than the Al chelates of unsubstituted 8HQ.

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The thermal behavior of chelates of rare earth metal with 8HQ and 5,7-dichloro derivatives was studied in air by Chang et al. [4]. These studies showed that the thermal stability of the ligand 8HQ is higher than that of 5,7-dichloro-8HQ. A literature survey reveals that no extensive study has been made of the thermal properties of chelates of oxine (8HQ) and their derivatives [1,3,4].

The major goal of the present investigation is to study the thermal behavior of chelates of both 8HQ and 8AQ (8-aminoquinoline) with copper(II) and possibly to understand the mechanism of thermal decomposition of these chelates in the solid state.

EXPERIMENTAL

Preparation of the copper complex of 8AQ

Hydrated copper chloride was reacted with 8AQ (pure chemical, Eastman Organic Chemicals, Canada) and recrystallized from an ethanol–distilled water solution (1 : 2). The product was then washed several times with absolute ethanol.

Preparation of the copper complex of 8HQ

A solution of copper chloride (0.01 mol) in ethanol was mixed with 0.02 mol of 8HQ (Cambrian Chemicals) in ethanol. The complexes thus formed were separated out as solids, then filtered off, washed several times with absolute alcohol, dried and kept in a vacuum desiccator.

Chemical analysis of the solid complexes obtained

Copper was estimated by EDTA titration [5]

$Cu \cdot C_9H_8N_2 \cdot Cl_2 \cdot 2H_2O$, calc.: Cu, 20.193%; found: Cu, 20.969%

$Cu(C_9H_6NO)_2$, calc.: Cu, 18.058%; found: Cu, 17.13%

Thermogravimetry (TG)

A Stanton automatic thermogravimetric balance was utilized in the temperature range 20 – 600 °C in air.

Differential thermal analysis (DTA)

A Netzsch automatic DTA system was employed and a Pt/Rh–Pt thermocouple was used in the temperature range 20 – 600 °C in air.

RESULTS AND DISCUSSION

TG results of 8AQ solid complex with $CuCl_2$ in air

Table 1 and Fig. 1 show the TG results of solid complex ($Cu \cdot 8HQ \cdot Cl_2 \cdot 2H_2O$) in the temperature range 20–600 °C. The TG results (Fig. 1) gave clear evidence that the complex has a great thermal stability up to 196 °C, when dehydration begins. This relatively high dehydration temperature supports the opinion that water molecules are coordinated to the copper ion, and are not just a part of the humidity water (physically combined water or moisture content). The first step of decomposition is the elimination of water molecules, ending at 224 °C. The second weight-loss step (224–262 °C) is most probably correlated with the elimination of the two chloride ions coordinated to the copper ion (as depicted from the present chemical analysis and spectral measurements). This is due to the relatively stronger chloride ion coordination, with the complex molecule, compared to the neutral water molecules. The third step is concerned with both the decomposition and oxidation of the solid metal chelate in the temperature range 262–440 °C, giving volatile carbon and metal oxide residue as the end product. The broad maximum and its subsequent end constancy (Fig. 1) support this explanation. Stoichiometric (quantitative) calculations from the obtained thermograms (Fig. 1) strongly confirm that the decomposition scheme can be represented as follows

$$Cu \cdot 8AQ \cdot Cl_2 \cdot 2H_2O \overset{186-224\,^\circ C}{\rightarrow} Cu \cdot 8AQ \cdot Cl_2 \overset{224-262\,^\circ C}{\rightarrow}$$

$$Cu \cdot 8AQ \overset{262-440\,^\circ C}{\rightarrow} CuO + (CO/CO_2;\ N_2/NO;\ NO_2)$$

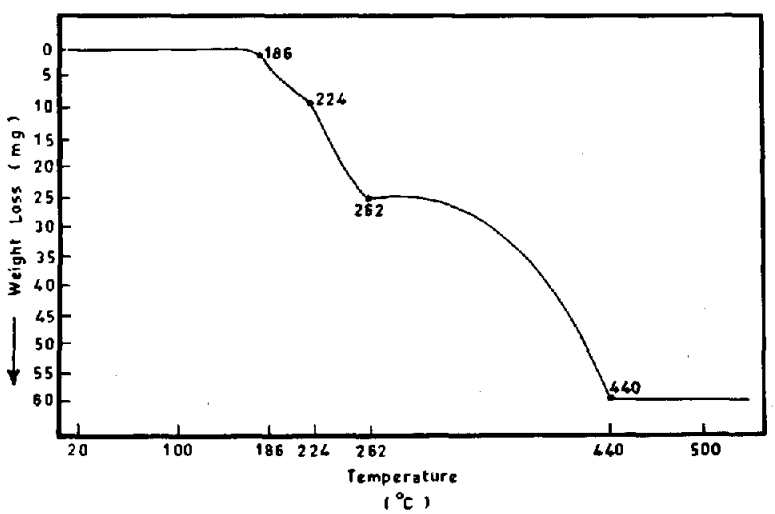

Fig. 1. TG curves of the solid $Cu \cdot 8AQ \cdot 2H_2O$ complex.

TABLE 1

Thermal behavior of the 8AQ complex with $CuCl_2$

Temp. (°C)	Sample weight observed (mg)	Sample weight calculated to fit the chemical formula (mg)	Chemical formula (established)	Mol. wt. (calculated)	Assignment
20–186	80	–	$Cu \cdot 8AQ \cdot Cl_2 \cdot 2H_2O$	314.054	Stable
186–224	71	70.839	$Cu \cdot 8AQ \cdot Cl_2$	278.623	Loss of chemically combined water
224–262	55	55.654	$Cu \cdot 8AQ$	217.717	Loss of Cl_2
262–440	21	20.251	CuO	79.539	Decomposition to metal oxide as end product

TABLE 2

Thermal behavior of the 8HQ complex with $CuCl_2$

Temp. (°C)	Sample weight observed (mg)	Sample weight calculated to fit the chemical formula (mg)	Chemical formula (established)	Mol. wt. (calculated)	Assignment
20–134	94.8	–	$Cu(8HQ)_2$	351.848	Stable
134–248	91.4	–			Partial sublimation
248–278	91.4	–			Sublimation ceased due to sintering
278–318	53.30	53.25	Remaining second ring portion (Fig. 3)	197.677	Dissociation of the first ring of the organic ligand
318–396	50.30	–			Partial sublimation
> 396					The beginning of decomposition of the remaining second ring of the organic ligand

TG results of the 8HQ complex with $CuCl_2$ in air

Depending on the method of preparation (metal analysis, UV and IR absorption spectra) the chemical formula of chelate complex of $CuCl_2$ with 8HQ is $Cu(8HQ)_2$. The TG curve of the precipitated and recrystallized complex (see Fig. 2) displays a weight loss at 134–248 °C which could be correlated with the partial sublimation of the complex. Quantitative calculation (see Table 2) indicated that, at 278–318 °C, the material investigated suffers a sudden weight loss which is most probably correlated with the decomposition of the first ring of the organic ligand. Above 396 °C, the decomposition of the remaining (second) ring of the ligand will obviously follow according to the well-defined schematical representation suggested in Fig. 3. These observations are further confirmed through quantitative calculations. The conclusions reached were in agreement with the earlier foundations of Majumdar and Paria [1] on studying the thermal analysis of the palladium complex with 2-methyl-8HQ. Both small and large differences occur between our results and those of earlier authors [1] for the temperature

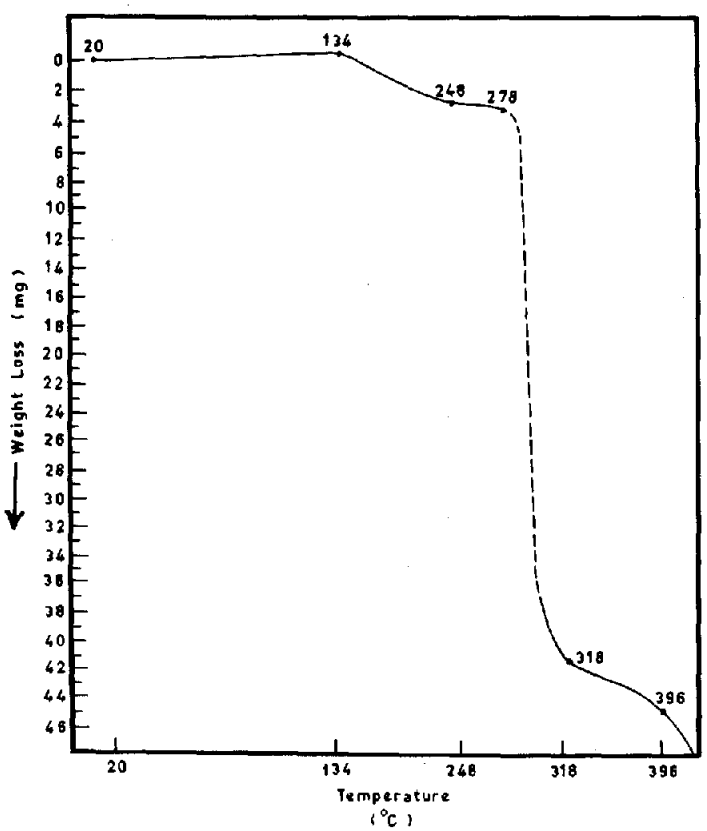

Fig. 2. TG curves of the solid $Cu(8HQ)_2$ complex.

at which the decomposition of the first- and second-ligand rings occurred. These are most probably correlated to the differences in the metal ion and substitution in the organic ligand molecules. In our opinion, the two steps of thermal decomposition, including the relatively low temperature at which the first organic ring begins to decompose, are attributed to the weak coordinating bonds of the first ring with respect to the relatively strong covalent bonds of the second-decomposed ligand ring. This observation is not considered for TG results of 8AQ due to its similar metal ligand coordinating bonds.

DTA of the copper(II) complex with 8HQ in air

For this complex (Fig. 4, Table 3) the slight detectable endothermicity at 134–220 °C is due to its slow partial sublimation (see the TG curve, Fig. 2). This is accompanied by a broad exothermic peak at 240 °C corresponding to the melting of the complex [6]. The two sharp endothermic peaks at 284 and 293 °C are most probably correlated with the vaporization of the complex, which often occurred after melting [6]. The two strong exothermic peaks situated at 306 and 366 °C are most likely due to the decomposition of the first ligand ring [1] (as depicted by the TG curves, Figs. 2 and 3) and lattice rearrangement [7], and/or second ligand ring, respectively (Figs. 3 and 4).

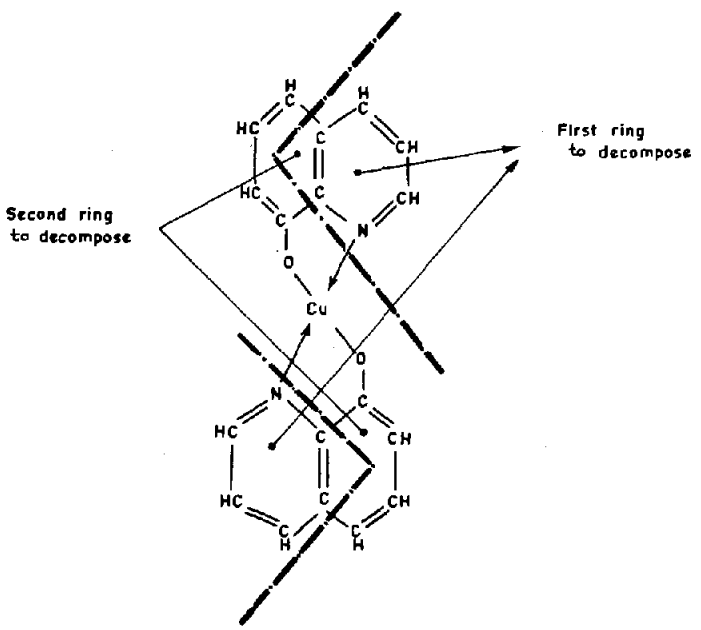

Fig. 3. Schematical representation showing the first and second thermally decomposed rings of the solid $Cu(8HQ)_2$ complex.

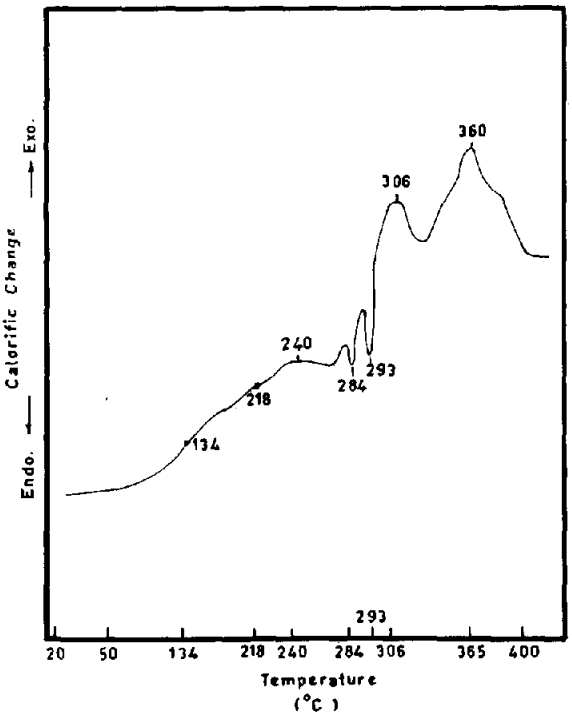

Fig. 4. DTA of the solid $Cu(8HQ)_2$ complex.

TABLE 3

DTA peaks and their assignments for the copper(II) complex with 8HQ

Temp. (°C)	Peaks	Assignment
20–134	No calorific change	Stability zone
134–218	Endothermic peak	Slow partial sublimation of the complex
240	Broad exothermic peak	Melting of the original complex
284	Sharp endothermic	Vaporization of the com-
293	peaks	plex after melting
306	Strong endothermic peak	Decomposition of the first organic ligand ring (see Fig. 3)
366	Strong exothermic peak	Lattice rearrangement

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